Field emission from amorphous-carbon nanotips on copper

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Amorphous-carbon (a-C) nanotips were directly grown on copper substrates by microwave plasma-enhanced chemical-vapor deposition. The length of a typical a-C nanotip is ~250 nm and its tip diameter is ~25 nm. The in-plane correlation length La, equivalent to the size of the sp^2 clusters, is determined to be 1.2 nm through the intensity ratio of the D and G peaks in the Raman spectrum, which is about in the optimum range for field emission. A low turn-on field of 1.6 V/μm at 10 μA/cm^2, a threshold field of 3.8 V/μm at 10 mA/cm^2, and a high current density of 32.42 mA/cm^2 at 4.0 V/μm are achieved. The field emission characteristics of a-C nanotips are close to those of carbon nanotubes, and much better than what has been reported for flat diamond-like carbon or a-C:H coated cathodes. The roles of the sp^2 cluster size, electron confinement and conductivity in the field emission of a-C nanotips are discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1620681]

I. INTRODUCTION

The search for excellent field emitters has attracted remarkable attention in the field of cold-cathode field-emission displays.[1–4] Excellent field emitters should provide channels of high conductivity for electrons to flow into vacuum. A high local field or a low energy barrier at the emission sites is also crucial for excellent field emitters according to the Fowler–Nordheim equation.[5] The carbon nanotube (CNT) is now recognized as the best carbon system for field emission because of the high local field at its extremely sharp tip[6] and high conductivity that is able to carry very large current density.[7] The typical turn-on field at 10 μA/cm^2 and threshold field at 10 mA/cm^2 are 0.1–1.0 and 1–2 V/μm, respectively.[8,9] Amorphous carbon (a-C) is another carbon system that is useful for field emission which has attracted attention since amorphous carbon can be deposited on large areas at low temperature.[10] Usually, a-C is defined as a mixture of sp^3, sp^2, and even sp^1 sites with the possible presence of up to 60% hydrogen.[11] Diamond-like carbon (DLC) (>50% sp^3)[12] and hydrogenated amorphous carbon (a-C:H) (40%–50% sp^3)[12] are two common a-C materials with a large amount of sp^2 bonds which are frequently used to fabricate flat a-C field emitters.[12–15] The flat a-C field emitter is thus sometimes called the flat DLC or a-C:H field emitter. The existence of the high local fields at emission spots of a flat a-C field emission surface has been realized by measurement of the electron energy distribution of the emitted electrons.[16] The most acceptable mechanism to account for the high local field at emission spots in the a-C film is the internal-tip mechanism.[12] Sp^2 conducting channels inside the a-C film act as internal tips, providing conductive paths for electrons flowing to the surface and emitted from surface at emission spots. However, the typical turn-on and threshold fields of flat a-C field emitters are 2–12 and 6–10 V/μm, respectively, about one order of magnitude higher than those of CNTs.[17–19] The difference is a result of the extremely sharp tip shape and high conductivity of CNT.[6,7] It is thus of interest to fabricate a-C nanotips with higher conductivity so that the field emission performance of a-C is greatly improved and close to that of CNTs.

In this article, we present the field emission characteristics of a-C nanotip structures grown on copper substrates. The turn-on and threshold fields of a-C nanotips are close to those of CNTs. The advantages of the a-C nanotip process are described in the following. First, the deposition is a low-temperature low-cost process. Second, uniform and well-aligned a-C nanotips of large area are easier to deposit without metal catalysts.

II. EXPERIMENTAL DETAILS

Copper sheets 0.5 mm thick were cleaned with acetone and de-ionized water and then put into a planar microwave plasma-enhanced chemical-vapor deposition (MPECVD) system. This plasma source is based on the excitation of a plasma surface wave. Details about the planar MPECVD system can be found in the literature.[20,21] Before the deposition of a-C, the chamber was first pumped to a base pressure of 5×10^{-3} Torr, and H_2/CH_4 with a flow rate of 47/14 sccm was fed into the chamber to ignite the H_2/CH_4 mixed plasma operated at 3000 W and 0.14 Torr. The a-C was then deposited onto the copper substrates at different bias voltages for 2 h at 200 °C. The morphologies and microstructures of the deposited samples were characterized by a JEOL JSM-6500F field-emission scanning electron microscope (FESEM) and by JEM-2010 transmission electron microscope (TEM), respectively. Chemical information on a-C

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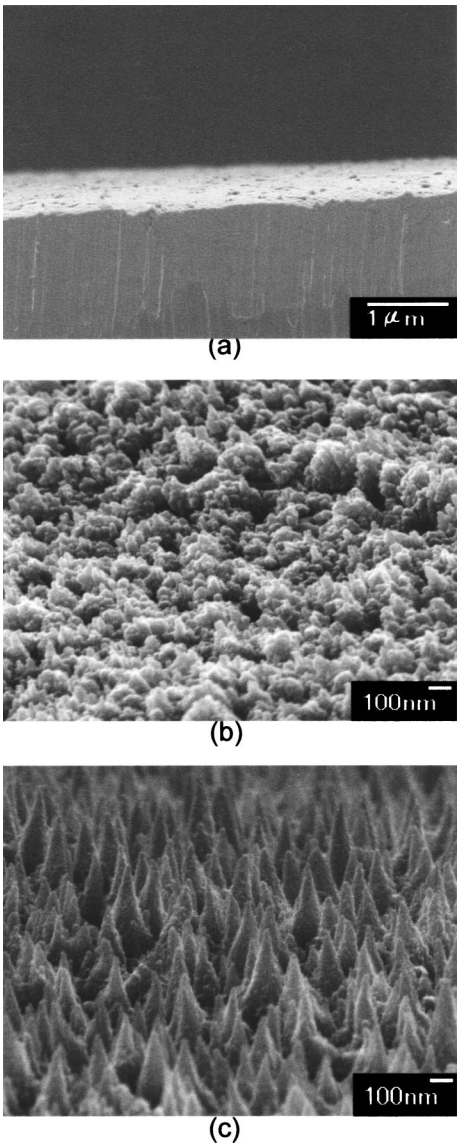

FIG. 1. Cross-sectional FESEM images of a-C deposited at different bias voltages: (a) -50, (b) -150, and (c) -250 V. The samples were tilted forward 5° during measurement.

nanotips was characterized by an energy dispersion x-ray (EDX) spectrometer of the FESEM. The field emission characteristics were measured at 7×10^{-7} Torr in a planar diode configuration at room temperature. The interelectrode spacing was 150 μm, defined by a spacer located outside the emission area, and the anode area was 0.986 cm^2.

III. RESULTS AND DISCUSSION

The growth of the a-C nanotip structure on Cu strongly depends on the bias voltage applied. When the copper substrate was biased at -50 V, no a-C was observed on Cu as shown in Fig. 1(a). A coral-like structure of a-C appears on the Cu substrate when the bias voltage is raised to -150 V. This suggests that a critical plasma potential is required for bias enhanced nucleation of a-C on Cu. The coral-like structure of a-C disappears and vertically aligned a-C nanotips

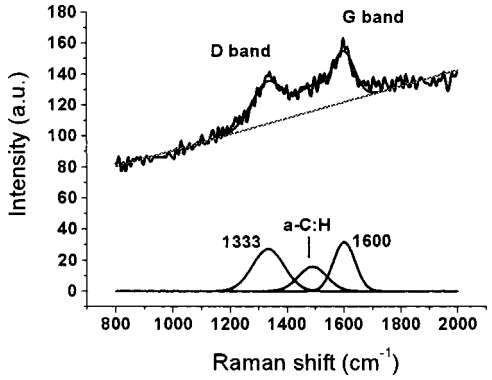

FIG. 2. Raman spectrum of a-C nanotips.

appear on Cu when the bias voltage is raised further to -250 V. It is likely that higher plasma potential favors growth of the nanotip structure of a-C.

The a-C nanotips in Fig. 1(c) are about 250 nm in height and conical in shape with their diameters ~90 nm at the bottom of the tips and ~25 nm at the top. The tip density is estimated to be 386 μm^{-2}. The bonding structures of a-C nanotips can be extracted from the Raman spectrum shown in Fig. 2. The spectrum shows two prominent peaks, D (1333 cm^{-1}) and G (1600 cm^{-1}), and a background peak (~1500 cm^{-1}) as indicated by the curve fit inserted in Fig. 2. The peak centered at about 1500 cm^{-1} is characteristic of the amorphous hydrogenated carbon (a-C:H)[12] frequently observed in plasma-enhanced chemical-vapor deposition using the CH_4/H_2 mixed plasma. The $E_{2g}G$ mode shifted from its normal value of 1580 to 1600 cm^{-1} is an indication of the existence of nanocrystalline graphite or sp^2 clusters.[11] The peak at 1333 cm^{-1}, close to the characteristic diamond peak at 1331 cm^{-1}, is assigned as $A_{1g}D$ mode rather than to diamond peak based on the following reasons. First, the breathing $A_{1g}D$ mode around 1350 cm^{-1}, a result of the presence of aromatic rings in disordered graphite, is always associated with the $E_{2g}G$ mode.[11] Second, the $A_{1g}D$ mode scatters in the range of 1200–1450 cm^{-1} for aromatic rings in disordered graphite inside the matrix of a-C:H.[22] Third, the width of the diamond peak at 1331 cm^{-1} should be around 3 cm^{-1}, much narrower than the 100 cm^{-1} of the observed D peak. Finally, the width of the D peak is about the same as that of the G peak. It is thus quite reasonable to assign the 1333 cm^{-1} peak to breathing $A_{1g}D$ mode.

Figure 3 shows the current density versus electric field ($J-E$) characteristics of a-C nanotips. The corresponding Fowler–Nordheim (FN) plot is shown as an inset in Fig. 3. The turn-on field to produce current density of 10 $\mu A/cm^2$ is as low as 1.6 V/μm and the threshold field to produce 10 mA/cm^2 is 3.8 V/μm. A high current density of 32.4 mA/cm^2 can be achieved at 4.0 V/μm. The field emission characteristics of a-C nanotips are close to those of CNTs and much better than what has been reported for flat a-C coated cathodes so far.[17–19]

The internal-tip mechanism has been proposed for flat a-C emitters in order to account for the observed field emission.[12] Sp^2 conducting channels act as internal tips inside flat a-C films, similar to the role of grain boundaries in

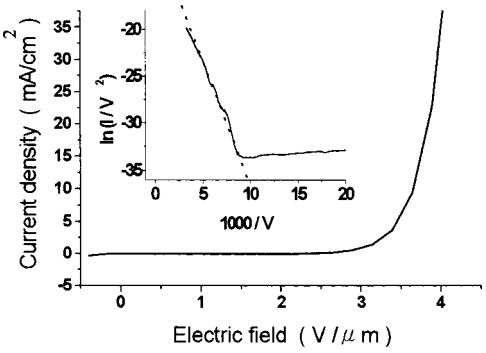

FIG. 3. Current density vs electric field ($J-E$) characteristics of a-C nanotips. A Fowler–Nordheim plot is included.

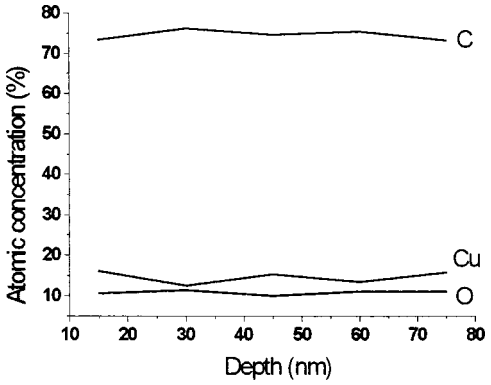

FIG. 5. Concentration profiles of Cu and O taken along a typical a-C nanotip by EDX FESEM. The depth is measured from the top of the nanotip.

nanocrystalline diamond films.[23] One parameter that can affect the field emission of a sp^2 conducting channel is the size of sp^2 clusters. The in-plane correlation length La, which describes phonon confinement in disordered crystals, is useful to characterize the size of sp^2 clusters. Llie *et al.*[3] reported that the optimum La value with the lowest threshold field is ~0.7–1.1 nm for a-C in the nanocrystalline graphite–amorphous carbon regime. The size of sp^2 clusters, equivalent to the diameter of the internal tip, is very close to that of a CNT. Similarly, the La value of the a-C nanotip, i.e., the diameter of the internal tip, is determined to be 1.2 nm by the intensity ratio of the D and G peaks, $I(D)/I(G)$, in the Raman spectrum in Fig. 3.[11] The La value derived is also very close to the diameter of a CNT.

The difference in field emission performance among CNTs, a-C nanotips and flat a-C films depends on the quality of the ''tip'' rather than the diameter of the ''tip'' alone. Electron confinement and conductivity are proposed to be two quality factors of the tip that affect field emission properties. Figure 4 schematically shows the electric field lines for a CNT, an a-C nanotip and a flat a-C film, taking into account the electron confinement along the tip. When electrons flow along the internal tip, i.e., the sp^2 conducting channel, inside the flat a-C film, they are partially confined since the energy band gap of a-C is about 2–4 eV only.[24] In contrast, the electrons flowing in a CNT are fully confined by the work function of CNT that is about 5 eV. CNTs thus have field emission characteristics that are superior to those of the flat a-C film since the field strength is much more intense at the top of the CNT. The a-C nanotip is expected to have poorer field emission than the CNT since its radius (~25 nm) is about an order of magnitude larger than that of the CNT. However, its field emission properties, such as turn-on and threshold fields, are close to published data for CNTs. The plausible explanation is the ''field shielding effect'' between nanotubes. Nillson *et al.* reported that most CNTs do not participate in emission when the mean separation between nanotubes is within two times the tube length.[25] In other words, only one CNT would dominate field emission within the shielding range. The field emission from an a-C nanotip would be dominated by one sp^2 conducting channel only since the diameter of the a-C nanotip is ~25 nm much less than twice the tube length.

One of the drawbacks of the flat a-C film is its low conductivity since a-C is a semiconducting material.[26] The conductivity of an a-C nanotip is expected to be improved by Cu diffusion at the a-C/Cu interface. The presence of Cu is evident in the concentration profile shown in Fig. 5 taken along a typical a-C nanotip by EDX FESEM. The Cu signal stays about the same inside the a-C nanotip and its atomic concentration is ~15%. This would tremendously improve the conductivity of the a-C nanotip. However, residual oxygen, with atomic concentration less than that of Cu, was also observed inside the a-C nanotip. This may partially reduce the conductivity contributed by Cu.

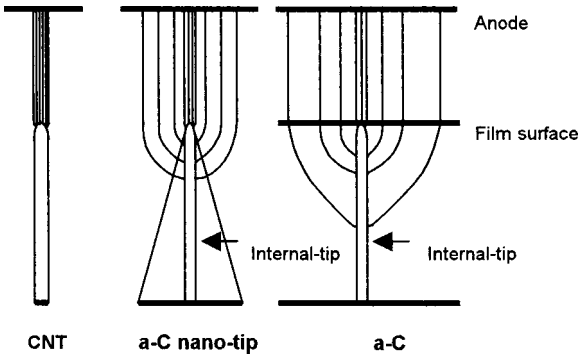

FIG. 4. Schematic of the electric field lines for a CNT, an a-C nanotip and a flat a-C film.

IV. CONCLUSIONS

A field emitter made of a-C nanotips on Cu was fabricated by planar microwave plasma-vapor deposition. A low turn-on field of 1.6 V/μm, a threshold field of 3.8 V/μm, and a high current density of 32.4 mA/cm^2 at 4.0 V/μm were achieved. The a-C nanotips enhance the field emission by more than one order of magnitude compared to flat a-C field emitters. The sp^2 conducting channels together with the tip shape and conductivity explain the enhancement of field emission well. The a-C nanotips process developed on Cu may deserve more attention in the search for excellent field emitters.

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